Contents

List of Contributors XIII
Preface XIX

1 Fundamental of Graphene 1
   Seong C. Jun
1.1 Introduction 1
1.2 Synthesis of Graphene 3
   1.2.1 Mechanical Cleavage 3
   1.2.2 Epitaxial Growth 4
   1.2.3 CVD Growth of Graphene 4
   1.2.4 Solution-Based Graphene 5
      1.2.4.1 Ultrasonication 6
      1.2.4.2 Intercalation 7
      1.2.4.3 Chemical Exfoliation 7
   1.2.5 Synthesis of Composite Material Based on Graphene
      Oxide 8
1.3 Characterization of Graphene 12
   1.3.1 AFM (Atomic Force Microscopy) 14
   1.3.2 SEM 16
   1.3.3 TEM/SEAD/EELS 16
   1.3.4 XPS 20
   1.3.5 XRD 21
   1.3.6 Raman 23
   1.3.7 Photoluminesces (PL) Measurement 23
1.4 Optical Property Modification of Graphene 25
   1.4.1 Absorption Property Modification of Graphene (Terahertz,
      UV–Visible–NIR) 25
      1.4.1.1 Absorption Property of Thermally Annealed Graphene
      Oxide 25
      1.4.1.2 Absorption Property Plasma Defected Graphene 26
   1.4.2 PL Property Modification of Graphene 29
      1.4.2.1 PL Properties of Oxygen Plasma Treated Graphene 29
      1.4.2.2 Substrate Effect 30
2 Graphene-Based Electrodes for Lithium Ion Batteries 49
Ronghua Wang, Miaomiao Liu, and Jing Sun
2.1 Introduction 49
2.2 The Working Principle of LIBs 50
2.3 Graphene-Based Cathode Materials for LIBs 51
2.4 Graphene-Based Anode Materials for LIBs 53
2.4.1 Graphene as Anodes for LIBs 54
2.4.2 Graphene-Based Composites as Anodes for LIBs 56
2.4.2.1 The Lithium Storage Mechanisms of Anode Materials 57
2.4.2.2 Graphene-Si/Sn Composites as Anodes for LIBs 58
2.4.2.3 Graphene–Metal Oxide Composites as Anodes for LIBs 62
2.4.2.4 Graphene–TiO$_2$/MoS$_2$ Composites as Anodes for LIBs 65
2.5 Two-Dimensional (2D) Flexible and Binder-Free Graphene-Based Electrodes 67
2.5.1 Graphene-Based Flexible Anode Materials for LIBs 67
2.5.1.1 2D Flexible and Binder-Free Graphene Electrodes 67
2.5.1.2 2D Flexible and Binder-Free Graphene-Based Hybrid Anode Electrodes 69
2.5.2 Graphene-Based Flexible Cathode Materials for LIBs 73
2.6 Three-Dimensional Macroscopic Graphene-Based Electrodes 74
2.7 Summary and Perspectives 78
References 79

3 Graphene-Based Energy Devices 85
Wei-Ren Liu
3.1 Introduction 85
3.2 Graphene for Li-Ion Batteries 85
3.2.1 Anode Materials 85
3.2.2 Cathode Materials 100
3.3 Graphene for Supercapacitors 105
3.4 Graphene for Li–Sulfur Batteries 111
3.5 Graphene for Fuel Cells 114
3.6 Graphene for Solar Cells 116
3.7 Summary 118
References 118

4 Graphene-Based Nanocomposites for Supercapacitors 123
Xuanxuan Zhang, Tao Hu, and Ming Xie
4.1 Introduction 123
4.2 Graphene-Based Supercapacitors 124
4.2.1 EDLCs 125
4.2.2 Graphene/Metal Oxide Nanocomposites 128
4.2.3 Graphene/Conducting Polymer Composites 129
4.2.3.1 PANI-Graphene Nanocomposites 129
4.2.3.2 PPy–Graphene Nanocomposite 132
4.2.3.3 PEDOT–Graphene Nanocomposite 134
4.2.4 Atomic Layer Deposition for Graphene/Metal Oxide Nanocomposites 134
4.3 Issues and Perspectives 136
References 138

5 High-Performance Supercapacitors Based on Novel Graphene Composites 145
Junwu Xiao, Yangyang Xu, and Shihe Yang

5.1 Introduction 145
5.2 Graphene Synthesis Methods 148
5.2.1 The “Top-Down” Approach 148
5.2.2 The “Bottom-Up” Approach 150
5.3 Graphene-Based Electrodes for Supercapacitors 151
5.3.1 Graphene 151
5.3.2 Graphene-Based Composites 152
5.3.2.1 Graphene–Carbon Material Composites 153
5.3.2.2 Graphene/Metal Oxide Composites 154
5.3.2.3 Graphene–Conducting Polymer Composites 158
5.3.2.4 Graphene/Metal Oxide–Conducting Polymer Composites 164
5.4 Conclusions and Prospects 165
References 166

6 Graphene for Supercapacitors 171
Richa Agrawal, Chunhui Chen, Yong Hao, Yin Song, and Chunlei Wang

6.1 Introduction 171
6.1.1 Electrochemical Capacitors 171
6.1.1.1 Fundamentals of a Capacitor 172
6.1.1.2 Classification of Electrochemical Capacitors 174
6.1.2 Graphene as a Supercapacitor Material 175
6.2 Electrode Materials for Graphene-Based Capacitors 176
6.2.1 Double-Layer Capacitance-Based Graphene Electrode Materials 176
6.2.1.1 Electrodes Based on Graphene Synthesized by Reduction of Graphene Oxide 176
6.2.1.2 Activated-Graphene-Based Electrodes 177
6.2.1.3 Graphene and Other Carbon Nanostructure Composite Electrodes 179
6.2.1.4 Nitrogen-Doped-Graphene-Based Electrodes 180
6.2.2 Graphene/Pseudocapacitive Material Composite Based Electrode Materials 183
6.2.2.1 Graphene/Conducting Polymer Composite Electrodes 183
6.2.2.2 Graphene/Transition-Metal Oxide Composite Electrodes 186
6.3 Graphene-Based Asymmetric Supercapacitors 189
6.3.1 Asymmetric Capacitors Based on Graphene and Pseudocapacitive Materials 193
6.3.2 Graphene-Based Lithium-Ion Capacitors 195
6.4 Graphene-Based Microsupercapacitors 199
6.5 Summary and Outlook 204
Acknowledgments 205
References 205

7 Graphene-Based Solar-Driven Water-Splitting Devices 215
Jian Ru Gong
7.1 Introduction 215
7.2 Basic Architectures of Solar-Driven Water-Splitting Devices 216
7.3 Promising Prospects of Graphene in Solar-Driven Water-Splitting Devices 217
7.4 Graphene-Based Integrated Photoelectrochemical Cells 219
7.5 Graphene-Based Mixed-Colloid Photocatalytic Systems 227
7.6 Graphene-Based Photovoltaic/Electrolyzer Devices 235
7.7 Conclusions and Perspectives 241
References 241

8 Graphene Derivatives in Photocatalysis 249
Luisa M. Pastrana-Martinez, Sergio Morales-Torres, José L. Figueiredo, Joaquim L. Faria, and Adrián M.T. Silva
8.1 Introduction 249
8.2 Graphene Oxide and Reduced Graphene Oxide 250
8.2.1 Synthesis 250
8.2.2 Properties 252
8.3 Synthesis of Graphene-Based Semiconductor Photocatalysts 254
8.3.1 Mixing Method 255
8.3.2 Sol–Gel Process 255
8.3.3 Hydrothermal and Solvothermal Methods 256
8.4 Photocatalytic Applications 257
8.4.1 Photodegradation of Organic Pollutants 258
8.4.2 Photocatalytic Splitting of H₂O 262
8.4.3 Photocatalytic Reduction of CO₂ 264
8.4.4 Other Applications: Dye-Sensitized Solar Cells 266
8.5 Conclusions and Outlook 267
Acknowledgments 268
References 268
9 Graphene-Based Photocatalysts for Energy Applications: Progress and Future Prospects 277
Wanjun Wang, Donald K.L. Chan, and Jimmy C. Yu
9.1 Introduction 277
9.1.1 Synthesis of Graphene-Based Photocatalysts 278
9.1.2 Ex Situ Hybridization Strategy 279
9.1.3 In Situ Growth Strategy 279
9.1.3.1 Hydrothermal Method 279
9.1.3.2 Electrochemical and Electrophoretic Deposition 281
9.1.3.3 Chemical Vapor Deposition 281
9.1.3.4 Photochemical Reaction 282
9.2 Energy Applications 283
9.2.1 Photocatalytic Hydrogen Evolution 283
9.2.2 Photocatalytic Reduction of Carbon dioxide 285
9.2.3 Environmental Remediation 286
9.2.3.1 Photodegradation of Organic Dyes 287
9.2.3.2 Water Disinfection 287
9.3 Conclusions and Outlook 287
References 288

10 Graphene-Based Devices for Hydrogen Storage 295
Hou Wang and Xingzhong Yuan
10.1 Introduction 295
10.2 Storage of Molecular Hydrogen 297
10.2.1 Graphene-Based Metal/Metal Oxide 299
10.2.2 Doped Graphene 300
10.3 Storage of Atomic Hydrogen Based on Hydrogen Spillover 301
References 304

11 Graphene-Supported Metal Nanostructures with Controllable Size and Shape as Advanced Electrocatalysts for Fuel Cells 307
Minmin Liu and Wei Chen
11.1 Introduction 307
11.2 Fuel Cells 308
11.2.1 Configuration and Design of PEMFCs 309
11.2.2 Direct Methanol Fuel Cells (DMFCs) 310
11.2.3 Direct Formic Acid Fuel Cells (DFAFCs) 313
11.2.4 Direct Alcohol Fuel Cells (DAFCs) and Biofuel Cells 314
11.3 Graphene-Based Metal Nanostructures as Electrocatalysts for Fuel Cells 315
11.3.1 Graphene-Supported Metal Nanoclusters 315
11.3.2 Graphene-Supported Monometallic and Alloy Metal Nanoparticles (NPs) 317
11.3.3 Graphene-Supported Core–shell Nanostructures 321
11.3.4 Graphene-Supported Hollow Nanostructures 322
11.3.5 Graphene-Supported Cubic Nanostructures 325
11.3.6 Graphene-Supported Nanowires and Nanorods 326
11.3.7 Graphene-Supported Flower-Like Nanostructures 329
11.3.8 Graphene-Supported Nanodendrites 331
11.3.9 Other Graphene-Supported 2D or 3D Nanostructures 333
11.4 Conclusions 333
Acknowledgments 334
References 335

12 Graphene-Based Microbial Fuel Cells 339
Yezhen Zhang and Jian S. Ye
12.1 Introduction 339
12.2 MFC 340
12.2.1 The Working Principle of MFC 340
12.2.2 The Advantages of MFCs 341
12.2.3 The Classification of MFCs 342
12.2.3.1 Dual-Chamber and Single-Chamber MFCs 342
12.2.3.2 Direct and Indirect MFCs 344
12.2.3.3 Heterotrophic, Photosynthetic Autotroph, and Sediment MFCs 344
12.2.3.4 Intermittent and Continuous MFCs 344
12.2.3.5 Pure Bacteria and Mixed Bacteria MFCs 345
12.3 The Development History of MFCs 345
12.4 The Application Prospect of MFC 346
12.4.1 Micro Batteries Embedded in the Body 346
12.4.2 Mobile Power Supply 346
12.4.3 Photosynthesis to Produce Electricity 346
12.4.4 Biosensor 347
12.4.5 Power Supply in Remote Areas or Open Sea 347
12.4.6 Treatment of Organic Wastewater 347
12.5 Problems Existing in the MFCs 348
12.6 Graphene-Based MFC 348
12.6.1 Anode 348
12.6.2 Membrane 350
12.6.3 Cathode 350
References 351

13 Application of Graphene-Based Materials to Improve Electrode Performance in Microbial Fuel Cells 355
Li Xiao and Zhen He
13.1 Introduction 355
13.2 Graphene Materials for Anode Electrodes in MFCs 357
13.2.1 Graphene Nanosheets 357
13.2.2 Three-Dimensional Graphene 359
13.2.3 Graphene Oxide 361
13.3 Graphene Materials for Cathode Electrodes in MFCs 361
Contents

13.3.1 Bare Graphene 362
13.3.2 Polymer Coating with Graphene as a Dopant 363
13.3.3 Metal Coating with Graphene as a Supporter 363
13.3.4 Nitrogen-Doped Graphene 364
13.4 Outlook 366

References 367

14 Applications of Graphene and Its Derivative in Enzymatic Biofuel Cells 371
A. Rashid bin Mohd Yusoff
14.1 Introduction 371
14.2 Membraneless Enzymatic Biofuel Cells 372
14.3 Modified Bioanode and Biocathode 375
14.3.1 Electrochemically Reduced Graphene Oxide and Multiwalled Carbon Nanotubes/Zinc Oxide 375
14.3.2 Graphene/Single-Walled Carbon Nanotubes 376
14.4 Conclusion 376
Acknowledgment 377
References 377

15 Graphene and Its Derivatives for Highly Efficient Organic Photovoltaics 379
Seung J. Lee and A. Rashid bin Mohd Yusoff
15.1 Introduction 379
15.2 Various Applications in Solar Cells 380
15.2.1 Conductive Electrodes 380
15.2.1.1 Transparent Conductive Anodes 380
15.2.1.2 Transparent Conductive Cathodes 384
15.2.2 Active Layer 385
15.2.2.1 Light-Harvesting Materials 385
15.2.2.2 Schottky Junctions 388
15.2.3 Charge Transport Layer 390
15.2.3.1 Hole Transport Layer 390
15.2.4 Electron Transport Layer 395
15.2.4.1 Interfacial Layer in Tandem Solar Cells 398
15.3 Conclusion 402
Acknowledgment 402
References 402

16 Graphene as Sensitizer 407
Mohd A. Mat-Teridi, Mohd A. Ibrahim, Norasikin Ahmad-Ludin, Siti Nur Farhana Mohd Nasir, Mohamad Yusof Sulaiman, and Kamaruzzaman Sopian
16.1 Graphene as Sensitizer 407
16.2 Graphene as Storage Current Collector 410
16.2.1 Anode Current Collector 411
  16.2.1.1 Li-Ion Storage 412
  16.2.1.2 Fuel Cells 412
16.2.2 Cathode Current Collector 413
  16.2.2.1 Li-Ion Storage 414
  16.2.2.2 Fuel Cells 414
16.3 Graphene as Photoanode Additive 415
  16.3.1 DSSC Application 415
  16.3.2 OPV Application 416
  16.3.3 Lithium-Ion Battery 417
  16.3.4 Sensor Application 418
  16.3.5 Transparent Conductive Films 419
  16.3.6 Photocatalytic Application 420
16.4 Graphene as Cathode Electrocatalyst 420
  16.4.1 N-Doped Graphene 421
  16.4.2 B-, P-, S-, and Se-Doped Graphene 422
16.5 Conclusions 423
Acknowledgment 424
References 424
Index 431